

**SOME EXPERIMENTS ON THE MANIFESTA-
TION OF OSMOTIC PRESSURE WITH
MEMBRANES OF CHEMICALLY
INERT MATERIALS**



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SOME EXPERIMENTS ON THE MANIFESTATION OF OSMOTIC PRESSURE WITH MEMBRANES OF CHEMICALLY INERT MATERIALS¹

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The direct observation of osmotic pressure requires the use of a so-called semipermeable membrane, the function of which has been the cause of much discussion among investigators interested in osmotic phenomena. When two bodies of matter are separated by a layer of a third which is of such a nature that the others pass through it at unequal rates, osmotic pressure results and the intermediate layer constitutes a semipermeable membrane. Usually the material on one side of the membrane is called the "solvent" and that on the other side the "solution." Generally the latter consists of a solution of some solute in the "solvent." Under suitable conditions, with the proper apparatus, the solvent passes more readily through the membrane into the solution until finally a state of equilibrium is reached when a certain pressure is developed in the solution which pressure is called osmotic pressure. Without the semipermeable membrane the solvent and solution merely diffuse into each other until a solution of uniform concentration is produced. No difference in pressure results. Generally speaking, the membrane "allows of a pressure being exerted on a solution in contact with a solvent, without exerting a pressure on the latter."²

Previous Work and General Theories Involved

While such is essentially the acknowledged function of the membrane the mechanism of its action is a matter of doubt. The theories in regard to it may be divided into two classes in which the membrane has respectively a passive and an active function in the phenomena. The former includes such

¹ The experiments described in this article were performed in the Chemical Laboratory of the Michigan Agricultural College Experiment Station and the results are published with the permission of the Director.

² Findlay: "Osmotic Pressure," p. 66 (1913).

theories as Traube's "atomic sieve" theory and Poynting's hydrate theory, while the latter includes the various solution theories, the electrostatic theories of Perrin and of Girard, etc.

The first detailed consideration of the passive function of the membrane was given by M. Traube,¹ who was the first investigator to use precipitation membranes. He conceived membranes to be sieve-like structures, the openings being molecular interstices (as distinguished from the pores of other membranes). He prepared membranes of various materials including the precipitate of gelatine and tannic acid, ferrocyanides of copper, iron, mercury and lead. Some of his attempts failed to yield precipitates capable of acting as membranes and to explain this in the light of his theory, he formulated the rule that "any precipitate whose interstices are smaller than the molecules of its components must assume the membrane form on contact of the solutions of its components."

He also clogged the pores of some of his membranes with other materials in order to reduce the size of the interstices. Such membranes varied in permeability and exhibited certain properties which substantiated his theory.

Ostwald² studied the permeability of membranes for ions in the light of Traube's theory. From his work it follows that a membrane is permeable for a salt only when it is permeable for *both* ions of that salt; and if a membrane is impermeable for an ion it is impermeable for all salts containing that ion.

Tammann,³ however, disproved the above statements and declared himself opposed to Traube's theory.

Likewise Walden⁴ after an exhaustive investigation of several precipitation membranes says (p. 718) "precipitation membranes cannot act as atomic sieves."

Pickering⁵ attempted to substantiate Traube's theory.

¹ "Arch. Anat. Physiol. und Wissen. Med.," 1867, p. 87.

² Zeit. phys. Chem., 6, 71 (1890).

³ Ibid., 10, 255 (1892).

⁴ Ibid., 10, 699 (1892).

⁵ Ber. deutsch. chem. Ges., 24, 3629 (1891).

He suggested that solute molecules possess a certain affinity by which they attract solvent molecules and hold them in a more or less unstable manner. These clusters of molecules pass through the pores of the membrane less readily than single solvent molecules.

This work was later discredited by Barlow¹ who demonstrated the defectiveness of the experimental methods upon which it was based.

The simple sieve theory has been more or less modified in the minds of later workers especially as regards the mechanism of its action. For instance Poynting² assumes a combination between solute and solvent molecules which decreases the mobility of the latter. His conception of osmosis is as follows: "The solvent molecules are entering the membrane from both sides, but the mobility or number set free per second from the pure solvent is greater than the number set free from the solution. The membrane goes on absorbing the solvent from each side till it becomes saturated, *i. e.*, holds so much that it returns as many molecules as it receives. It is receiving more from the pure solvent side, and therefore when saturated for that side is supersaturated for the other. Consequently more molecules are sent into the solution than are received from it, and the solution grows until the growing pressure so much increases the mobility that it is equal on both sides of the membrane."

Later Larmor³ while believing that "each molecule of the dissolved substance forms for itself a nidus in the solvent; that is, it sensibly influences the molecules around it up to a certain minute distance, so as to form a loosely connected complex in the sense not of chemical union but of physical influences" still criticized Poynting's theory as follows: "that Prof. Poynting's recent suggestion with a view to evading the necessity of the ionic dissociation hypothesis, cannot

¹ Phil. Mag., [6] 10, 1 (1905); Findlay and Short: Jour. Chem. Soc., 87, 819 (1905).

² Ibid., [5] 42, 289 (1896).

³ Nature, 55, 545 (1897).

avail, as it would not lead to the desired value for the osmotic pressure; the pressure depends on the number of molecular complexes involving the dissolved substance that exists in the dilute solution, but not on their individual degrees of complexity."

Still another variation of the sieve theory is that of Sutherland¹ who states that "if we seek to picture to ourselves how a membrane allows water molecules to pass, but not sugar molecules, our simplest conception of its structure is that of a mesh, amidst the threads of which the water molecules are packed in such a manner as to give way before one another almost as in ordinary water, while the sugar molecules are held back by the mesh. Thus the mesh forms a solid or quasi-solid framework through which water can pass with high viscous resistance, while the sugar molecule is absolutely blocked. Now if the framework turns back the sugar molecules, it must take the force of their blows and shield the water molecules from them. If then we suppose a semipermeable membrane separating water and a dilute solution of sugar in water the sugar molecules are to be regarded as replacing some water molecules, but their collisions on the water in the membrane are rendered inoperative by the shielding action of the framework so that the water molecules in the membrane receive more impacts on the side of the pure water than on the side of the solution and therefore water flows through the membrane until in the solution there is enough excess of hydrostatic pressure established to compensate for the inoperative impacts of the sugar molecules. This inequality of pressure which can be hydrostatically balanced is the osmotic pressure."

M. Traube's conception of the action of the semipermeable membrane was subjected to emphatic adverse criticism by J. Traube² who cites the work of Overton.³ Overton

¹ *Phil. Mag.*, [5] **44**, 493 (1897).

² *Ibid.*, [6] **8**, 704 (1904).

³ *Zeit. phys. Chem.*, **22**, 189 (1897); *Vierteljahreschr. d. Naturf. Gesellsch. Zurich*, **40**, 1 (1895); **44**, 88 (1899).

showed that permeability increased in homologous series by the substitutions of CH_3 , for H, C_2H_5 for CH_3 , etc. This was contrary to M. Traube's hypothesis which postulated that an increase in the size of the molecule should cause a decrease in the readiness with which a substance should pass through a membrane.

Also Barlow¹ after demonstrating the defects in Pickering's work states that "It may justly be concluded that these experiments prove that the part played by the membrane in osmotic phenomena is not a sieve-like one." He claimed that pure alcohol passed through a copper ferrocyanide membrane easier than pure water although when these two are separated by such a membrane the water flows into the alcohol.

Kahlenberg² also opposes the sieve theory. He says: "When we think of a large molecule like that of copper oleate rapidly travelling through vulcanized caoutchouc as in No. 35, and that under like conditions cane sugar, AgNO_3 , and LiCl do not pass through the septum, it certainly must convince us that the membrane does not act as a sieve."

Finally in connection with this theory attention may be called to the recent work of Tinker³ who examined with the ultramicroscope, precipitation membranes made according to Traube. He says (p. 368): "Since the smallest pore diameter in a copper ferrocyanide membrane is about 8 millimicrons, it follows that from 100 to 200 water molecules could be placed in a chain from one side of such a pore to the other, and the several thousand could be travelling across the cross section of the pore at the same time. A selective mechanical blocking of even large hydrated crystallized molecules is hence out of the question, and this hypothesis for accounting for osmotic effects—already largely rejected—is no longer tenable."

A second series of theories ascribing a more active part to the membrane, assign to it a capillary structure. Chrono-

¹ Loc. cit.

² Jour. Phys. Chem., **10**, 169 (1906).

³ Proc. Royal Soc., **92A**, 357 (1916).

logically this was apparently the first to be advanced. From subsequent articles it seems probable that Fisher¹ must have had this conception of the organization of the membrane. Likewise Poisson² attempted to show that osmosis was due to capillarity rather than electric action as suggested by Dutrochet. The latter denied that capillarity could explain the phenomenon although he later³ stated distinctly that osmotic phenomena were observed when two liquids were separated by a membrane with capillary pores.

Draper⁴ states emphatically his belief in the capillary structure of osmotic membranes and gives details of his conception of the action of such a membrane.

The real development of this theory, however, dates from an article by Brücke.⁵ He devised a cell consisting of a glass tube pressed against a glass plate and obtained osmotic effects through the crack thus formed.⁶ He attributed the results to the difference in the attraction of the walls of the capillaries for the two liquids and explained in detail the mechanism of the action. Evidence tending to confirm his views was contributed later by Ludwig⁷ who showed that membranes actually did take up less solution than solvent. Fick⁸ discusses both of these articles at some length. He does not, however, favor the capillary theory. Some years later Baranetzky⁹ investigated the relations between membranes of parchment, bladder, cellulose and collodion and the quantities of various salts taken up by them and claimed to have added experimental proof for Brücke's theory.

Pfeffer,¹⁰ after a thorough consideration of the whole

¹ Gilberts Ann., 72, 298 (1826); see also Pogg. Ann., 10, 481; 11, 126 (1827).

² Pogg. Ann., 11, 134 (1827).

³ Ann. Chim. Phys., 49, 412 (1832).

⁴ Jour. Franklin Inst., 17, 177; 18, 27 (1836).

⁵ Pogg. Ann., 58, 77 (1843).

⁶ See also Fischer (Loc. cit.) and Dutrochet (Ann. Chim. Phys., 35, 393 (1827); 49, 411 (1832)) for osmosis through cracks in glass.

⁷ Pogg. Ann., 78, 307 (1899).

⁸ Ibid., 94, 59 (1855).

⁹ Ibid., 147, 195 (1872).

¹⁰ "Osmotische Untersuchungen," Leipzig (1877).

subject, expressed himself as favoring the capillary theory.

Moore¹ attempted to show that osmosis "may be produced by difference in surface tension acting along the exceedingly fine capillary openings of almost molecular dimensions which place the solution in connection with its solvent in the pores of the semipermeable wall which separates them." He says: "It seems reasonable to suppose that after such a process (the precipitation of a membrane) communication takes place only in the intramolecular spaces or meshes of the precipitate."

The work of Tinker² may again be cited in connection with the capillary theory. He measured, microscopically, the sizes of the particles composing the precipitation membranes made from the same materials that Traube used and found a distinct connection between the diameters of the membrane pores, as calculated from the sizes of the particles, and the osmotic activity of the various membranes. He says (p. 370): "The relation between the extent to which the capillaries of a membrane are controlled by the surface forces and the osmotic properties of the membrane is, however, an apparent and noteworthy one. Copper ferrocyanide and Prussian blue—the most perfect of membranes—have their pores completely under control; the tannate and silicate membranes, which are not so efficient, have a central space within their capillaries throughout which the surface forces are comparatively weak, while membranes such as gelatin and parchment, which are permeable to all crystalloids, have pores which possess central canals outside the surface force range."

The capillary theory, as Bigelow³ has pointed out, serves as a compromise between the strictly mechanical "sieve" theory and the purely chemical "solution" theory. This last theory ascribes to the membrane a still more active part in the process of osmosis. It postulates that a membrane is permeable to such substances as are soluble in it and imper-

¹ *Phil. Mag.*, 38, 279 (1894).

² *Loc. cit.*; see also Pfeffer: "Osmotische Untersuchungen," p. 43.

³ *Jour. Am. Chem. Soc.*, 29, 1675 (1907).

meable to those which are not. This theory, now probably the most generally accepted one, was anticipated by Liebig¹ as early as 1848 when he said: "The volume changes of two miscible liquids which are separated from each other by a membrane depends upon the unequal wetting or attraction which the membrane exerts on the two liquids."

In view of Liebig's own assertion later that his conception of osmosis appeared to be identical with Graham's it is certainly permissible to interpret "Anziehung" in a broad enough way to include "attraction of solution" in which case we have an exact statement of the present-day conception of the solution theory.

While Liebig's statement must be considered as exceedingly significant in view of later developments, the first important experimental work performed with the object of substantiating such a theory was carried out some years later by L'hermite.² He appears to have had a very clear idea of the possible relations between osmotic phenomena and solution and capillarity. He was the first to use the "three liquid layer" means of demonstrating that one liquid, soluble in a second liquid, will pass into it through a layer of a third liquid in which the first is more soluble than the second. He pointed out the significance of this experiment from the standpoint of osmotic phenomena.

At almost the same time Graham in a series of articles dealing with the diffusion of liquids under various conditions formed practically the same idea of the process of osmosis, though his statements were hardly as clear nor were his experiments as conclusive, in the light of later work, as were L'hermite's. For instance in his early work³ he found that the most pronounced osmotic effects were obtained with acid or basic substances while neutral salts and organic compounds were inert or showed very weak effects. This appears to

¹ "Uarschen der Säftebewegung," Braunschweig (1848); also Liebig's *Ann.*, **121**, 78 (1862).

² *Ann. Chim. Phys.*, [3] **43**, 420 (1855).

³ *Phil. Trans.*, **144**, 177 (abs. in *Phil. Mag.*, [4] **8**, 151 (1854)).

have been the basis for the formation of his first theory that osmosis depended on the interaction of the membrane and the liquids bathing it. In this article he opposes the capillary explanation of osmosis since he was unable to obtain results with membranes of various materials which he knew to be porous. Later he seems to have approached more nearly the pure solution theory as he says:¹ "The separation described (sugar from gum arabic by dialysis) is somewhat analogous to that observed in a soap bubble inflated with a gaseous mixture composed of carbonic acid and hydrogen. Neither gas, as such, can penetrate the water film. But the carbonic acid, being soluble in water, is condensed and dissolved by the water film, and so is enabled to pass outwards and reach the atmosphere, while hydrogen being insoluble in water, or nearly so, is retained within the vesicle." Although this statement was made in regard to the process of dialysis, it is certainly suggestive of the tendency of thought, especially in view of his explanation of osmosis with aqueous solutions and colloidal membranes which he gives on p. 222 of the same article. "It now appears to me that the water movement in osmose is an affair of hydration and dehydration in the substance of the membrane or other colloidal septum." And on p. 223, "Placed in pure water, such colloids are hydrated to a higher degree than they are in neutral saline solutions. Hence the equilibrium of hydration is different on the two sides of the membrane of an osmometer. The outer surface of the membrane being in contact with pure water tends to hydrate itself to a higher degree than the inner surface does, the latter surface being supposed to be in contact with a saline solution. When the full hydration of the outer surface extends through the thickness of the membrane and reaches the inner surface it there receives a check. The degree of hydration is lowered, and water must be given up by the inner layer of the membrane, and it forms the osmose."

Nernst² describes a "three liquid layer" experiment

¹ Phil. Trans., 151, 183 (1861).

² Zeit. phys. Chem., 6, 37 (1890).

similar to those first performed by L'hermite which he used to illustrate the action of an osmometer. He separated ether from a solution of ether in benzol by a parchment membrane saturated with water, the water constituting the intermediate liquid layer or "membrane."

Tammann,¹ after citing experimental evidence against Traube's sieve theory, calls attention to the work of L'hermite and Nernst and definitely compares precipitation membranes to their three liquid layers, saying (p. 263), "In exactly the same manner one can also explain the semipermeability of precipitation membranes. . . . Whether any substance, other than water, can pass through the membrane depends only upon its solubility in the membrane (the third liquid layer)."

The same idea of the function of the membrane in narcosis was held by Overton.² His assumptions were later contradicted by J. Traube.² Likewise, Barlow,³ working with gutta percha membranes and solutions of lithium chloride and camphor, decided "that for osmotic pressure to show itself, the membrane must be able to dissolve the solvent and have a distinct 'attraction of solution' for it."

Wilcox⁴ concluded that experiments in osmosis are merely distribution experiments, thereby reiterating the views expressed some fifty years previous by Schumacher⁵ who said (p. 338), "If we examine somewhat more closely the processes of endosmosis we can easily persuade ourselves that they are nothing more than distribution phenomena (*Mischungerscheinungen*)."

Also in his statement on p. 339, that in order to be miscible the substances must possess a certain degree of chemical attraction, Schumacher anticipates a somewhat modified form of the solution theory which has recently been proposed by Kahlenberg² who has described many experiments in support of his ideas. Kahlenberg assumes not

¹ *Zeit. phys. Chem.*, **10**, 255 (1892).

² *Loc. cit.*

³ *Phil. Mag.*, [6] **11**, 595 (1906).

⁴ *Jour. Phys. Chem.*, **14**, 576 (1910).

⁵ *Pogg. Ann.*, **110**, 337 (1860).

merely a solution of the liquids in the membrane but a loose chemical combination. He says, "In this paper it has been shown that whether osmosis will take place in a given case or not depends upon the specific nature of the septum and the liquids that bathe it; and if osmosis does occur, these factors also determine the direction of the main current and the magnitude of the pressure developed. The motive force in osmotic processes lies in the specific attractions or affinities between the liquids used, and also those between the latter and the septum employed. These attractions or affinities have also at times been termed the potential energy of solution, etc. They are to the mind of the writer essentially the same as what is commonly termed chemical affinity."

In this connection Nelson¹ says: "This view (*i. e.*, 'The Chemical or Selective Theory') of the nature of osmosis carries with it the assumption of a labile compound formed between the membrane and the solvent on the one hand and between the solvent and the solute on the other, and ascribes the movement of liquid into the osmotic cell by assuming that the solute robs the membrane of its imbibed solvent, the membrane in turn imbibing more solvent which is again extracted by the solute, this process being repeated until equilibrium is established. . . . It is only by assuming a chemical attraction and loose chemical combination that these results become at all intelligible. The mechanism of the formation of such a labile chemical compound between the membrane and the solvent on the one hand, and the solvent and the solute on the other, cannot be conceived of simply as a 'solution' of solvent and solute in the membrane when that word merely implies an orderly filling of the membranous interstices or intermolecular spaces by solvent or solute by virtue of capillary attraction."

While Kahlenberg was guided in his work by L'hermite's experiments, most of his investigations were conducted with rubber membranes and organic solvents.

His methods and some of his conclusions were subjected

¹ Jour. Am. Chem. Soc., **35**, 658 (1913).

to severe criticism by Cohen and Commelin¹ who however were interested in his data more from the standpoint of its relation to van't Hoff's theories of osmosis than from his ideas of the action of the membrane.

Although the preceding brief review of the theories concerning the functions of the membrane in osmotic pressure phenomena is not complete, some details and minor variations having been omitted it nevertheless gives concise statements of these theories and affords an idea of the main lines along which they have developed. A careful study of the subject leads one to agree with Fitzgerald that "the theory of semipermeable diaphragms is in a very doubtful state." In recent years serious consideration of the purely mechanical sieve theory seems to have been eliminated and the field left to the various explanations based upon solutions or chemical attraction and capillarity. A more detailed, critical discussion of these two will be taken up later. Suffice it to say here that while most of the results obtained by Kahlenberg were perhaps predicable, *a priori*, the assertion that they might serve as a basis for a general theory of the function of all semipermeable membranes appeared doubtful. The exact nature of the "labile compound" between the solvent and the membrane seemed to be anything but definite, and the assumption that a chemical combination between membrane and solvent was always a requisite for osmosis seemed hardly to be justified by the data presented.

In order to test this assumption, the experiments described in this paper were carried out, the intention being to obtain osmotic effects under such conditions as to preclude the possibility of chemical reaction between the membrane and the solvent. While it may be unsafe, in view of the various new types of compounds which modern chemistry has either discovered or invented to harmonize with its theories, to claim that no chemical action can take place between water and gold or carbon under ordinary circumstances, it must still be considered as a rather remote possibility.

¹ Zeit. phys. Chem., **64**, 1 (1908).

Materials

The materials used in the preparation of the membranes were selected with the object of securing substances which would be as inert as possible toward the liquids with which the membrane would come in contact, since, as has already been stated, the object of the work was to obtain osmotic effects under conditions which should preclude as far as possible any chemical reaction between the membrane and cell contents. For the same reason it was necessary that the materials should be exceptionally pure. Consequently all substances used in preparing membranes were carefully purified before use.

The following materials were chosen from which to make membranes: silica, carbon (graphite and amorphous), metallic copper, metallic silver and metallic gold. They were all in a state of fine powders with the exception of one sample of graphite and the gold, which were in the form of small flakes or plates. For use they were pressed into discs in the cells, these discs constituting the membranes.

Apparatus

Owing to the peculiar physical nature of the materials, *i. e.*, the fact that they were in the form of powders, special apparatus and technique had to be developed for the construction of the membranes. The type of cell finally adopted was patterned after that used by Bigelow and Bartell¹ in working with unglazed porcelain. It consisted of the following parts: (Fig. 1.) A base (A) for holding the membrane; a plate (B) covering the open side of the base to hold the membrane in place; a second plate (C) for holding the glass parts of the cell against the base; an attachment (D) for use in connecting the cell to the pressure tank and gauge for measuring pore diameters and saturating the membranes, threaded rods G, G, G, and nuts for holding the various parts together. The base and plate (B) were made of manganese bronze and all other metal parts of yellow brass. A cell

¹ Jour. Am. Chem. Soc., 31, 1194 (1909).

similar in construction but about five-sixths as large, and made entirely of brass with the parts held together by screws was first used. This cell was not strong enough to stand either the pressures used in forming the membranes or to hold the parts together with firmness enough to prevent leakage. Also the screws were less satisfactory than the threaded rods and nuts. Two plungers (E and F) exactly fitting the cavities in the base were used in forming the membrane (see p. 115). For measuring pore diameters the cells were connected with a pressure tank and gauge through capillary brass tubing fitted with brass unions. The three pieces of apparatus, cell, gauge and gas tank were connected through a specially constructed

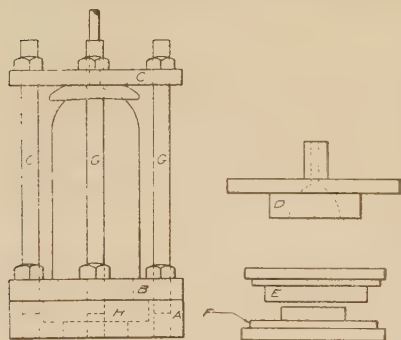


Fig. 1

brass T. The gauge was an accurate one graduated to 30 kilograms per cm^2 and reading directly to 0.25 kilogram per cm^2 . The tank was a small oxygen tank with a valve capable of delicate adjustment. It was charged with pure nitrogen from a large tank holding fifty cubic feet.

These cells were used for membranes of all materials with the exception of metallic gold. Owing to the expense of preparing such a large membrane of this material, an attachment was designed which fitted the cavity in the base of the large cell and in effect reduced the size of this cavity. This attachment was made of brass, gold-plated. Suitable plungers, also gold-plated, were made to form the membrane in this modified base.

Much time was lost in attempting to make the gold membrane in a glass tube. Tubing of various sizes was tried, including that used in making high pressure gauges. This had a diameter of 30 mm with a bore of 12 mm. None withstood the pressure required to make the membrane of sufficient density to show osmotic effects.

In the early part of the work a good grade of rubber packing was used for the washers required to make the cells tight. It was noticed on taking apart cells which had stood for some time that this packing had swelled. This was objectionable since it would have a tendency to produce apparent osmotic effects by causing an increase in the volume of the cell contents. Also it was found that, on long contact under pressure, it caused a corrosion of the bronze parts of the cells and a discoloration of the surfaces of the metallic membranes. Since any such chemical action might produce soluble impurities which would give the very condition least desired, these washers were later replaced with filter paper saturated with paraffine. In the final form of cell the glass parts were ground to the metal and washers were entirely eliminated at these points.

In the early part of the work, the glass part of the cell consisted of a tube 40 mm in diameter and about 50 mm long held between the plates B and C, and filled with the solution under investigation. The opening in plate C was closed with a one-holed rubber stopper holding the manometer tube and the whole cell was set in a beaker of distilled water. In this way one side of the membrane was bathed with the

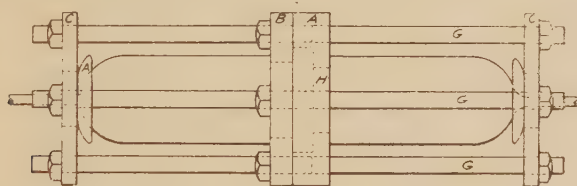


Fig. 2

solution and one side with distilled water. Although this arrangement was used throughout in saturating the membranes, measuring pore diameters, etc., it was found necessary later to change it in setting up the cells for observation in order to have equal volumes of liquid on each side of the membrane. Also continual trouble was experienced with the rubber stoppers leaking or changing their shape. To obviate these difficulties, the cell was set up as shown in Fig. 2. In

this form the manometer tube was sealed to the large tube holding the liquid. The glass parts were held against the base as before by the plate C and protected from breakage through contact with it by means of the washers of rubber packing, KK. Instead of setting the cell in a beaker of water, the water was held in exactly the same sort of arrangement as was the solution, but against the opposite side of the cell base. The manometer tubes were bent at right angles to the long axis of the cell which was given a horizontal instead of a vertical position. The effect was that of a U-tube with the membrane at the bottom.¹ As the level of the liquid rose in one arm, it fell in the other. In addition to the advantages already cited this cell made it possible to detect any change in volume of the apparatus or its contents due to leakage, change in volume of the membrane, change in volume of the solution on dilution, formation of gas, etc. It has proven entirely satisfactory in every respect.

Preparation of Membranes²

Several methods of preparing the membranes were tried. The first one was by means of the centrifuge.³ A high powered machine, capable of developing a speed of over 3000 r. p. m. and having a radius of 30 cm was used. A circular perforated plate of copper (H) was placed in the cell base covering the lower opening. This plate rested on a washer to prevent leakage between the membrane and cell. It was covered with a disc of ordinary filter paper⁴ to prevent the material passing

¹ U-shaped cells have been used by Vierordt: *Pogg. Ann.*, **73**, 519 (1848); Raoult: *Zeit. phys. Chem.*, **17**, 737 (1895); *Comptes rendus*, **121**, 187 (1895); Lord Berkeley and Hartley: *Proc. Roy. Soc.*, **73**, 436 (1904); Barlow: *Phil. Mag.*, [6] **11**, 596 (1906); Bartell and Hocker: *Jour. Amer. Chem. Soc.*, **38**, 1043 (1916).

² As this work was nearing completion, an article by W. Spring (*Zeit. phys. Chem.*, **2**, 532 (1888)) was found which discussed the compression of powdered materials. The author's experiences with metallic substances, silica, kaolin, clay, etc., agree in general with those of Spring.

³ See Lynde: *Jour. Phys. Chem.*, **16**, 763 (1912).

⁴ Hardened parchment paper cannot be used as it alone will give osmotic effects.

through the perforations in the plates. The base was then placed in the centrifuge cup, a suspension of the material poured in the cup whirled. This method was used only with silica, before a press was tried, and proved wholly unsatisfactory.

Next, the cell base, fitted with perforated plate and filter paper as above, was used as a suction filter and the cavity filled with material before centrifuging. This procedure alone, however, was no more successful than the former.

The first successful membranes were made by filling the base with material by sucking a suspension into it, then clogging the pores by the addition of a suspension of very fine material of the same kind which did not settle for some time. The plungers E and F were placed in position and the membrane compressed by means of a mechanical press. The first press used was an ordinary letter press. Since there was no way of measuring the pressures used and inasmuch as only comparatively low pressures could be obtained, the chance to use a hydraulic press of the Büchner type was welcomed and this was used in all subsequent work.

A third method of procedure which gave very satisfactory results with some materials was to fill the cavity with the dry powder. The first portion was pressed at a pressure considerably lower than that to be finally used. The pressure was released at once, the cell removed and a second portion of material added. This was pressed at a somewhat higher pressure and the process continued till the desired thickness had been obtained. In some cases in order to avoid the subsequent separation of the layers with the consequent formation of air spaces, it was necessary to moisten each one before the addition of a fresh portion of the powder. In this way less material was squeezed out around the plunger. Also with some materials it was more convenient to work with the dry powder than to try to get a suspension.

In all cases after the formation of the membrane it was covered with a piece of filter paper, perforated plate and washers and held in place by the plate B. The perforated

plate was necessary to prevent the rupturing of the membrane during saturation, measurement of pore diameters and washing.

The glass tube used to hold the water for saturating the membrane was next placed in position. In the first experiments this was just small enough in diameter to fit into the opening in the plate B and rested against a washer on the metal plate supporting the membrane. Owing to the fact that in some cases the membrane was slowly distorted by the pressure required to make the contact water-tight, a tube with a larger diameter was afterwards substituted. This rested against the plate B and thus removed all possibility of disturbing the membrane. The tubes used in this part of the work were approximately 50 mm long and 40 mm in diameter. They were held between the plates B and C by means of the nuts on the threaded rods, leakage being prevented by washers of rubber packing.

The next step was the saturation of the membrane. When it was sufficiently porous this was done by suction as the air could be more completely displaced by this means than by forcing it out with pressure. A high vacuum pump directly connected to the cell, or a gas tank evacuated by means of the pump, was used to draw the water into the membrane. Brass T tubes, attached to the cells through one-holed rubber stoppers inserted in the opening in the plate C and connected with each other and the pump by means of heavy-walled suction tubing, made it possible to saturate several membranes at once. The distilled water used in saturation was held in heavy glass jars in which the cells were placed. Frequently it was necessary to use membranes so dense that suction failed to draw water through them. The cells containing these were filled with water and attached to the pressure tank and gauge used for the measurement of pore diameters and the water forced through the membranes at as low a pressure as possible. This pressure ordinarily was between four and eight kilograms per cm^2 , though in a few cases it was higher. From one to two hundred cc of water

were forced through each membrane before it was considered to be saturated.

Measurement of Pore Diameters

When the membrane was saturated the diameters of the largest pores were measured according to the method used by Bigelow and Bartell.¹ This consisted in connecting the cell supported with the bottom up, to the pressure tank and gauge, covering the surface of the membrane with water and gradually increasing the pressure, noting that at which bubbles appeared through the openings in the plate. This pressure represents that required to displace the water in the pores by air. From it, by means of Jurin's law, the pore diameters can be calculated. This law may be formulated as follows: $a^2 = hr$ where a^2 is a constant (14.823 for water at 20°), h the height to which water would rise on account of capillarity and r the radius of the pore. The appropriateness of the method has been discussed by Bigelow and Bartell.

The results given in the following experiments represent the diameters of the largest pores only. In following the procedure outlined above the pressure was gradually increased until bubbles were issuing from about one-third of the total number of openings in the plate covering the membranes.

After measuring the diameters of the pores, the membranes were again saturated. In the early part of the work the cells were at once filled with solution and set up. Certain anomalous results were obtained, however, which seemed to indicate that the process of saturation left the membrane in a state of strain. Its readjustment caused changes in the volume of the cell which obscured the results due to osmosis. In subsequent work the membranes were allowed to stand several days before setting up and then were tested with water on both sides before filling the cell with solution.

Preliminary Experiments

Before going to the trouble of carrying out all the precautionary measures which it was realized from the first

¹ Loc. cit.

would have to be employed before final measurements could be made, it seemed desirable to determine whether or not any positive results at all could be obtained with the type of membrane and the materials which had been selected. With this in mind the preliminary experiments described in the following pages were conducted.

Silica.—Several samples of silica from various sources were investigated. The first positive effects were obtained with a sample prepared from sodium silicate by precipitation with HCl, washing free from Cl' and ignition. It contained 97.85 percent SiO_2 . With $M/1$ sugar solution it gave a corrected¹ reading of 28 mm at the end of 114 hours.

No measurements of the pore diameters were made on this membrane as it was prepared before the necessary apparatus had been obtained.

*Carbon.*²—The four samples of carbon which were used had the following characteristics:

No. 1 was a commercial graphitic powder 59.39 percent of which was lost on ignition.

No. 2 was a graphitic lubricant sold under the trade name of "Aquadag." When ignited 99.06 percent was volatilized.

No. 3 was a sample of carbon prepared by igniting cane sugar. It was completely volatilized on ignition but an analysis made by the Dennstedt combustion method showed it to contain 96.05 percent C and 100 percent H. Probably

¹ The observed readings with the vertical type of cell had to be corrected for two factors, *i. e.*, the capillary ascension of the liquid in the measuring tube and the greater density of the sugar solution as compared with water. For the tubing used in these experiments the algebraic sum of these two corrections, the former of which would tend to increase the true reading and the latter to lower it was calculated to be 6 to 8 mm. for $M/1$ sugar solution.

With the U-shaped cell, the capillarity factor in the correction disappears because the levels of both water and solution are measured in tubes of equal diameters. The correction for the difference in densities of the sugar solutions and water for the lengths of the columns of liquid representing the initial readings in all experiments with these cells were as follows: $M/2$ solution 9 mm, $M/1$ solution 17 mm, and 2 M solution 31 mm.

² Graham (Phil. Trans., 1854, p. 177) attempted without success to obtain osmotic effects with a membrane of compressed charcoal.

the impurities consisted of adsorbed gases or vapors as will be shown later.

No. 4 was a sample of commercial graphite which was in the form of small flakes. It gave a loss on ignition of 90.64 percent.

The following are the final corrected readings obtained with membranes of these materials and $M/1$ sugar solution:

TABLE I

1	25 mm	3	86 mm
2	58 mm	4	35 mm

The last membrane was also tested with 2 M sugar solution and gave a corrected reading of 110 mm.

The membrane prepared from sugar carbon was the first one on which pore diameter measurements were made. The first measurements showed an average pore diameter of 2.361 microns for the largest pores. No osmotic effects could be obtained. The cell was taken apart, the membrane pressed and again measured. The diameter of the largest pores then approximated 1.976 microns. The sugar solutions remained at the level of the water in the beaker indicating one of two things, either the membrane was too dense to allow the solution to flow through and assume the lower level which it should on account of its greater density, or a small osmotic pressure was produced. The next compression of the membrane reduced the pore diameters to 1.482 microns at which the above effects were noted.

Metallic Copper.—The material of which the first membranes were constructed was that used in making striping bronzes. It was an exceedingly fine powder and was supposed to be pure copper. The preliminary work was carried out on this assumption without making an analysis. Later an analysis showed it to contain only 95.76 percent Cu. This result is probably explainable by the fact that most commercial metallic powders are coated with stearin. For the later work this was almost completely removed by extraction with petroleum ether.

A membrane was prepared from this material and pressed till the pore diameters approximated 1.602 microns. It gave a final corrected reading of 20 mm with $M/1$ and 35 mm with 2 M sugar solution.

Metallic Silver.—The material used for this membrane was so-called "molecular silver" prepared according to Gomburg and Cone¹ from pure silver chloride.

The silver chloride was purified by repeated solution in ammonia and precipitation with HCl. After washing thoroughly with hot water it was placed in a glass crystallizing dish in which was also set a porous cup holding some pieces of granulated zinc. This cup was supported above the silver chloride by means of a glass triangle. A piece of platinum foil to which was attached a platinum wire was slipped under the silver chloride, and the free end of the wire was fastened to a piece of the zinc in the porous vessel. Distilled water was then added to both dishes, the level in the outer one being maintained somewhat above that of the inner one to lessen the outward diffusion of the zinc chloride. A few drops of HCl were also added to hasten the reaction. When the reaction appeared to be complete, the silver was removed, washed with ammonia to remove any unreduced silver chloride and then with hot water.

That used for the first membrane was not analyzed but from the method of preparation it undoubtedly was very pure. It was pressed into the cell base at a pressure of 250 kg per cm². Measurements showed the largest pores to be approximately 0.659 micron in diameter. When set up with $M/1$ sugar solution it gave a maximum corrected reading of 12 mm. Further pressing at 300 kg per cm² for three hours reduced the pore diameters to about 0.296 microns, after which a reading of 28 mm with $M/1$ sugar solution was obtained.

Metallic Gold.—The material was obtained in the form of nuggets from a manufacturer of dental supplies and was supposed to be pure. It was dissolved in aqua regia. A small residue was left which proved to be silver chloride. The

¹ Ber. deutsch. chem. Ges., 39, 3286 (1906).

liquid was decanted off and the precipitate transferred to a filter and washed, the washings being added to the original mother liquor. The resulting solution was concentrated and the precipitate, if any was formed, was removed as before. This process was repeated till no more material came down. The nitric acid was removed and the metallic gold precipitated by means of pure oxalic acid in the presence of ammonium oxalate. It was not analyzed but from the method of preparation was assumed to be pure.

The membrane was formed between perforated plates of gold in the modified cell described above. The gold, including the potatoes, weighed 21.08 g and was 6 mm thick. In the formation it was pressed at 40 kg per cm² but the pores were too large to measure. No positive results were noticeable.

The membrane was alternately pressed and set up with *M*/1 sugar solution until the pore diameters had been reduced to 2.361 microns when a maximum reading of 11 mm was obtained. Further pressing at 100 kg per cm² for ten minutes reduced the pore diameters to 1.695 microns, at which point a reading of 197 mm was recorded. The level of the solution was apparently still rising but it became necessary to take the cell apart and the maximum value was not obtained. This membrane was later subjected to further pressure which caused a corresponding reduction in the measurable pore diameters. The final readings taken are given in the following table:

TABLE II

Pore diameters	<i>M</i> /2 sugar solution	<i>M</i> /1 sugar solution	2 <i>M</i> sugar solution
0.847 micron	13 mm	32 mm	68 mm
0.741 micron	14 mm	17 mm	103 mm

The above results are considered to be accurate and, except where noted, free from the influence of certain sources of error discovered during the performance of this preliminary work. They manifestly justified the labor of repeating the

work, taking all the precautions necessary to insure thoroughly reliable results. Since the manipulation and method of procedure developed are for the most part new in their application to the study of osmotic phenomena, a more detailed discussion of the difficulties involved and of possible sources of error may not be out of place. Some of them are involved in the study of all membranes and all must be considered in dealing with membranes prepared from powdered or finely divided solid particles. For a more thorough consideration of the effects of some factors, especially temperature, upon osmotic processes, the reader is referred to the work of Morse and his co-workers, published in Publication No. 198 of the Carnegie Institute of Washington.

Factors Affecting Accuracy of Results

The following sources of error were observed in the preliminary work and guarded against as thoroughly as possible in the following experiments:

1. Changes in temperature.
2. Changes in volume of cell parts.
3. Changes in volume of cell contents.
4. Chemical reaction between materials used.

Changes in temperature: Temperature changes may produce errors in three ways, *i. e.*, by causing changes in the volumes of the solutions or of the parts of the cell or by causing a change in the rate of osmosis. Of these, the first is the only one of importance in these experiments because the range of temperature change was restricted to that of the room which would not produce a perceptible effect from the change in volume of parts of the cell, and the rate of osmosis was secondary though interesting. To remove error due to the first, the experiments were conducted in a thermostat, the temperature of which was held constant at $24.6 \pm 0.1^{\circ}$. This was, however, only large enough to hold the cells themselves. The measuring tubes projected above the water in the thermostat and consequently were exposed to changes in the room temperature. For the size of tube used and the

usual height of column of liquid exposed, this factor, from careful observation, was found to produce an error of only about 3 mm under extreme conditions. This is too small to influence the final values of any of the experiments though it might be responsible for incongruities in two consecutive readings.

Change in volume of cell parts: Errors may arise from this cause on account of change in volume of the membrane; change in shape of the membrane causing corresponding changes in the volumes of the parts of the cell holding the liquids; and changes in the volumes of rubber stopper or washers.

Changes in volume and shape of the membrane may result from pressure applied in its formation, saturation and measurement. These effects in some cases were rather significant and to avoid any error arising from them, all membranes were allowed to stand at least 24 hours before setting up. They were also tested by filling both parts of the cells with water and allowing to stand until the levels in the measuring tubes remained constant.

No measurements were made of the changes due to disintegration of the rubber stoppers and washers used in the earlier part of the work, but from the appearance of some of them the effects might have been considerable. As has been previously stated, rubber parts were eliminated entirely in the later work so that this source of error does not concern the following results:

Changes in volume of cell contents: Errors may be introduced on account of evaporation, drainage from measuring tubes after filling the cells, changes in temperature, hygroscopicity of solutions and increase or decrease in volume of solutions with dilution. Experiments made to measure the magnitude of such errors showed them to be very small.

No loss due to evaporation could ever be detected except in one or two experiments conducted incidentally, in which the liquids nearly filled the tubes. This condition did not exist in any of the experiments included in this report.

The method of filling the cells necessitated the filling of the measuring tubes with liquid above the zero level of the experiment. This excess liquid was removed by means of a capillary tube when the levels in the two measuring tubes were equalized. When this was done rapidly the subsequent drainage caused the levels to rise a few mm just as the reading of a burette or pipette changes if either is emptied too rapidly. This error was eliminated by drying the inner surfaces of the tubes with absorbent cotton attached to a fine wire or by readjusting the levels after drainage had ceased.

The effect of hygroscopicity and increase in volume of solution on dilution were imperceptible in the results reported in this paper but were of sufficient magnitude to attract attention in certain experiments conducted incidentally. The effect of either becomes evident as an inequality in the changes of levels in the two measuring tubes. In either case the level of the solution rises faster than the level of the water sinks—providing of course that the diameters of the measuring tubes are equal.

Chemical reactions between materials used: Errors from this cause fall into two classes, those which may produce apparent changes in volume of the liquid contents of the cells and those which may give rise to negative osmotic effects as described later.

Two important ones of the first class were met with: first, fermentation with the liberation of carbon dioxide and, second, the production of hydrogen through the interaction of water and finely divided metals used in making membranes. When either of these occurred the gas production caused unequal changes in the liquid levels making it appear that the volume of the liquid was changing. Both are easily detected by the formation of bubbles. Fermentation did not occur in any experiments included in this article. The formation of hydrogen was observed when membranes were made of finely divided zinc and iron. Since it was obvious that no results which would be of value could be obtained under such circum-

stances, attempts to obtain osmosis with membranes of these metals were abandoned.

In spite of all the precautions taken to avoid reactions between the various cell parts, the greatest difficulty encountered during the whole work arose from this cause.

Among the materials used in the construction of membranes was kaolin, with which attempts were made to duplicate the work of Bartell¹ on negative osmose. The solution used was $M/10$ $MgCl_2$ and very pronounced negative effects were observed.

Later in trying to obtain data on the extent of deformation of the membranes under various pressure treatment, kaolin membranes were set up with water both inside of the cell and in the beaker, *i. e.*, on both sides of the membrane. In all cases there was a flow of liquid from the cell to the beaker. The obvious explanation in this case was that the membrane was somewhat soluble in pure water and since the volume of water in the cell was smaller than that in the beaker, a more concentrated solution was formed which gave a condition analogous to that in which the cell was filled with the $MgCl_2$ solution.

At this time similar experiments were being tried with copper membranes. Strange to say, similar results were obtained. The abnormal readings were small and at first were disregarded, being attributed to various things such as temperature changes, leakage, evaporation and other causes which were later demonstrated to be insignificant. However, several readings were obtained which were of such magnitude that it became evident that some undetermined force was at work. Every precaution conceivable was taken to obviate the errors which have been discussed but still the negative results were obtained. The conclusion was finally forced upon us that even with the copper membrane, negative osmose was possible, and that the difference in the volumes of water on the opposite sides of these membranes was causing it to operate through the production of solution of different concentra-

¹ Jour. Am. Chem. Soc., 36, 646 (1914).

TABLE III

Date	Time	T	No. 3 Cu	No. 4 Cu	No. 10 Cu	No. 13 Cu	No. 20 Cu	No. 2 Kaolin	No. 5 Kaolin	No. 14 Kaolin
3/25	5 P.M.	22° C	0	0	0	0	0	—	—	—
3/26	4 P.M.	21	-8	+10	-7	-4	-7	—	—	—
3/27	10 A.M.	21	-8	-13	-10	-2	-7	—	—	—
3/29	9 A.M.	21	-8	-20	-15	-4	-5	—	—	—
3/30	1 P.M.	23	-11	-23	-20	-3	-5	—	—	—
3/30	3 P.M.	24	0	0	0	0	0	0	0	0
3/31	9 A.M.	20	-5	-9	-5*	-5	-5	0	-30+	-13
3/31	3 P.M.	22	-4	-7	0	-3	-1	+2	-11	-13
4/1	9 A.M.	21	-7	-12	-3	-6	-3	0	-30+	-19
4/2	9 A.M.	20	-11	-17	-7	-7*	-5	0	-30+	-24*
4/3	9 A.M.	19	-12	-19	-10	-7*	-4*	-1	-29*	-11
4/4	9 A.M.	20	-14	-24*	-12	-3	-3	0	-24*	-18
4/4	9 A.M.	22	-14	-4	-15	-4	-1	-4	-23*	-22
4/5	9 A.M.	23	-15	-7	-17	-5	-1	-3	-23*	-27
4/6	9 A.M.	19	-20	-16	-24*	-9	-4	-11	-27*	-13
4/7	9 A.M.	22	-16	-16	-25*	—	—	-10	-20*	-18
4/8	9 A.M.	22	-20	-20	-4	—	—	-10	-24*	-26
4/9	9 A.M.	22	-20	-24	-9	—	—	-15	-23*	-10
4/10	9 A.M.	18	-24*	-30+	-30*	—	—	-23*	-30+	-28*
4/12	11 A.M.	19	-3	-1	-5	—	—	-2	-16	-8
4/13	9 A.M.	19	-6	-5	-8	—	—	-4	-30+	-15*
4/14	9 A.M.	21	-10	-10	-10	—	—	-7	-24	-23
4/15	9 A.M.	21	-13	-15	-15	—	—	-9	-30+	-28*
4/16	11 A.M.	20	-16	-16	-20	—	—	-12	-18	-8
4/17	9 A.M.	20	-18	-23	-27	—	—	-13	-30+	-23
4/19	9 A.M.	20	—	—	—	—	—	—	—	—

* Set at 0 after this reading.

tions. To test this, two membranes which showed negative values were measured by Professor Bartell to determine the difference in electrical potential between opposite faces of the membranes. These measurements gave values of 0.1899 and 0.1605 volt, with the orientation that would be expected, *i. e.*, the "solution" side or inside of the membrane positive.

The above table shows some of the values obtained with eight different membranes, five of copper and three of kaolin. They are not at all quantitative since the minimum reading obtainable with the apparatus used was about -30 mm. When this point was reached it was necessary to raise the level to 0 by the addition of water. The experiments were carried out at room temperatures which are given in Column T. The readings are in mm and are uncorrected.

It will be observed that the results with the copper membranes were, as a rule, much smaller than those with kaolin and that in some cases a minimum was apparently reached. There are indications of a relation between the magnitudes of these results and the pore diameters as is shown by the following table, the values for which are taken from Table III:

TABLE IV

Cell No.	4	10	3	20	13
Pore diameters in microns	0.847	0.988	1.186	1.299	1.482
Observed reading 3/30 1 P.M.	-23	-20	-11	-5	-3
4/3 9 A.M.	-19	-10 ¹	-12	-4	-7

The above described conditions were responsible for the development, at the suggestion of Professor Bartell, of the U type of cell used in all subsequent work. With this the volumes of liquid on both sides of the membrane were approximately equal and any solution of the membrane took place to the same extent on both sides.

¹ Cor. reading = -15 as it was set back to 0 after 25 hours.

SOME EXPERIMENTS ON THE MANIFESTATION OF OSMOTIC PRESSURE WITH MEMBRANES OF CHEMICALLY INERT MATERIALS II¹

BY S. L. BIGELOW AND C. S. ROBINSON

Final Experiments with Membranes of Pure Materials

The complete success attending the attempts thus far described to obtain osmotic effects with inactive materials of widely different chemical natures made it seem improbable that the results could be entirely due to the small quantities of impurities present. We therefore concluded that it would be worth while to repeat the preliminary experiments using all the precautions found necessary to obviate possible errors. These final results are given in the following pages.

Silica: The material was prepared from a commercial sample of chemically pure silicic acid. It was first dehydrated in a platinum dish over a blast lamp, then pulverized in an agate mortar, washed with hot water several times by decantation and finally filtered with suction. After being dried in the oven and again thoroughly ignited it analyzed as follows:

0.6342 g subst. : 0.0003 g residue : 99.95% SiO_2

The membranes prepared from it were made by alternately pressing at 350 kg per cm^2 and clogging the pores by sucking a suspension of fine material through the membranes. Two membranes were prepared in this way and tested for osmotic effects after each treatment. When the largest pores had been reduced in size to 1.4823 microns (No. 3) and 0.3488 micron (No. 9), respectively, the results shown in the tables were obtained.

¹ The experiments described in this article were performed in the Chemical Laboratory of the Michigan Agricultural College Experiment Station and the results are published with the permission of the Director.

TABLE 5
No. 3
M/2 sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
1/27	0	9	1/31	14	23
1/28	9	18	2/ 1	14	23
1/29	14	23			

M/1 sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
1/12	0	17	1/20	42	59
1/13	—2	15	1/21	45	62
1/14	5	22	1/22	49	66
1/15	13	30	1/23	51	68
1/16	21	38	1/24	53	70
1/17	27	44	1/25	54	71
1/18	32	49	1/26	55	72
1/19	37	54			

2/*M* sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
2/2	0	31	2/10	78	109
2/3	15	46	2/11	78	109
2/4	35	66	2/12	79	110
2/7	66	97	2/14	79	110
2/8	71	102			

No. 9

M/2 sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
2/15	0	9	2/25	48	57
2/16	4	13	2/26	51	60
2/17	11	20	2/28	55	64
2/18	17	26	2/29	56	65
2/19	24	33	3/ 1	57	66
2/21	35	44	3/ 2	57	66
2/23	43	52			

M/1 sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
1/27	0	17	2/ 4	64	81
1/28	9	26	2/ 7	64	81
1/29	21	38	2/ 8	83	100
1/31	40	57	2/10	89	106
2/ 1	46	63	2/11	91	108
2/ 2	52	69	2/12	94	111
2/ 3	58	75	2/14	96	113

2 *M* sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
3/ 3	0	31	3/12	163	194
3/ 4	24	55	3/13	172	203
3/ 6	64	95	3/14	181	212
3/ 8	100	131	3/16	201	232
3/ 9	117	148	3/18	218	249
3/10	133	164	3/20	232	263
3/11	147	178	3/21	236	267 ¹

¹ The maximum reading with this membrane and solution could not be obtained because the level of the liquid on the water side sank into the cell.

At the conclusion of the above experiments the cells were taken apart, washed and pressed at 350 kg. per cm² after clogging the pores. The membrane in No. 9 was so cracked by this treatment that it was useless for further work. The diameters of the largest pores in No. 3 were slightly reduced. The following results were obtained with it:

TABLE 6
No. 3
M/2 sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
2/27	0	9	3/ 8	42	51
2/29	6	15	3/ 9	45	54
3/ 1	13	22	3/11	49	58
3/ 2	18	27	3/12	52	61
3/ 4	28	37	3/14	54	63
3/ 5	34	43	3/15	55	64
3/ 6	36	45	3/17	56	65

M/1 sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
3/17	0	17	3/30	140	157
3/19	19	36	3/31	147	164
3/21	45	62	4/ 2	159	176
3/24	85	102	4/ 4	168	185
3/25	96	113	4/ 6	175	192
3/27	115	132	4/ 7	178	195
3/28	123	140	4/10	185	202

2 M sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
4/10	0	31	4/20	175	206
4/11	10	41	4/22	201	232
4/12	30	61	4/24	222	253
4/13	52	83	4/26	241	272
4/14	74	105	4/28	257 ¹	288
4/16	114	145	5/1	277	308 ¹

It will be observed that in the first series, No. 9, having smaller pore diameters than No. 3 gave larger values, and that after the diameters of the pores in No. 3 had been reduced the values obtained with it were larger than before.

Carbon

Aquadag: The material after being acidified and washed was digested with aqua regia. After again washing, it was dried and ignited. This process was carried through twice, after which it was digested in a platinum dish with hydrofluoric acid, washed and again ignited.

A sample weighing 0.5880 g. was then burned to constant weight of residue. The residue weighed 0.0022 g corresponding to a loss on ignition of 99.63% of the sample.

Two membranes were made from this material. The largest pores showed diameters of the following order of magnitude:

No. 9 = 0.593 micron. No. 14 = 0.624 micron

The membranes were first set up with water on both sides. No movement of the liquid was noticeable. One side of each cell was then filled successively with $M/2$, $M/1$ and 2 M sugar solution and placed in the thermostat. The following corrected results were obtained:

¹ Maximum reading not available owing to liquid sinking into the cell on water side.

TABLE 7
M/2 sugar solution
 No. 9

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
6/12	0	9	6/14	7	16
6/13	5	14	6/15	7	16

No. 14

5/ 8	0	9	5/11	—46	—37
5/ 9	—16	—7	5/12	—48	—39
5/10	—37	—28	5/13	—46	—37

M/1 sugar solution
 No. 9

6/15	0	17	7/ 6	46	63
6/16	8	25	7/ 8	48	65
6/19	16	33	7/11	52	69
6/21	24	41	7/14	55	72
6/23	30	47	7/17	58	75
6/26	31	48	7/19	60	77
6/28	35	52	7/22	62	79
6/30	38	55	7/26	64	81
7/ 3	41	58	7/27	68	85

No. 14

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
5/19	0	17	5/24	9	26
5/22	4	21	5/25	10	27
5/23	6	23	5/27	11	28

2 M sugar solution

No. 9

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
8/ 1	0	31	10/6	103	134
8/ 4	6	37	10/12	109	140
8/ 8	13	44	10/18	117	148
8/10	17	48	10/24	125	156
8/12	20	51	10/30	133	164
8/16	27	58	11/ 5	141	172
8/23	39	70	11/11	146	177
8/28	48	79	11/17	152	183
9/ 2	57	88	11/24	159	190
9/ 9	70	101	11/29	165	196
9/13	78	109	12/ 5	169	200
9/22	95	126	12/ 9	160	191
9/30	99	130			

No. 14

5/31	0	31	6/20	127	158
6/ 2	22	53	6/22	131	162
6/ 4	47	78	6/24	133	164
6/ 6	66	97	6/27	140	171
6/ 8	81	112	6/29	143	174
6/10	93	124	7/ 1	145	176
6/13	107	138	7/ 5	150	181
6/15	113	144	7/ 7	151	182
6/17	119	150	7/10	153	184

The membranes were next washed out with water and again subjected to a pressure of 350 kg per cm². They were tested with water alone without showing any signs of osmotic effects, after which they gave the following results:

TABLE 8
M/2 sugar solution
 No. 9

The results of this portion of the experiment are without value because of the development of a leak in the cell. Through an oversight the work was not repeated.

No. 14

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
8/4	0	9	8/10	—37	—28
8/5	—1	8	8/11	—39	—30
8/8	—29	—20	8/12	—39	—30
8/9	—34	—25			

M/1 sugar solution
 No. 9

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
6/16	—8	9	7/ 6	46	63
6/19	16	33	7/10	50	67
6/21	24	41	7/13	54	71
6/23	30	47	7/15	56	73
6/26	37	54	7/18	59	76
6/28	35	52	7/21	61	78
6/30	38	55	7/24	63	80
7/ 1	39	56	7/26	64	81
7/ 3	41	58	7/28	65	82

No. 14

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
10/ 2	0	17	11/ 7	37	54
10/ 6	5	22	11/11	39	56
10/10	12	29	11/15	40	57
10/14	17	34	11/20	41	58
10/18	21	38	11/24	42	59
10/22	26	43	11/28	43	60
10/26	29	46	12/ 1	43	60
10/30	32	49			
11/ 3	35	52			

2 M sugar solution

No. 9

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
8/ 2	1	32	7/30	99	130
8/ 5	7	39	10/ 4	101	132
8/ 8	13	44	10/10	107	138
8/11	19	50	10/18	117	148
8/14	25	56	10/28	131	162
8/23	39	60	11/ 7	143	174
8/30	52	83	11/17	152	183
9/ 9	70	101	11/28	164	195
9/13	78	109	12/ 5	169	200
9/22	95	126	12/ 9	160	191

No. 14

12/ 5	0	31	1/11	152	183
12/ 8	18	49	1/14	158	189
12/11	35	66	1/17	166	197
12/14	50	81	1/20	174	205
12/17	63	94	1/23	180	211
12/20	75	106	1/26	188	219
12/23	87	118	1/30	197	228
12/30	113	144	2/ 2	203 ¹	234
1/ 2	124	155			
1/ 5	132	163			
1/ 8	143	174			

Sugar charcoal: For this work carbon was prepared from sugar by the following method which differs from that used in the preliminary work in that more care was taken to prevent the introduction of impurities and in the substitution of an alcohol burner for the gas burner used before. The

¹ Further readings were impossible owing to the liquid sinking into the cell.

sugar was placed in a silica dish and thoroughly charred. The crusty mass was then removed and finely powdered in an agate mortar. It was returned to the silica dish and re-ignited, during which process it was constantly stirred with a platinum wire so that all parts of the mass were raised to a dull red heat. It will be recalled that the product obtained before was apparently impure as indicated by its analysis by the combustion method. The suggestion was made at that time that these impurities consisted of adsorbed oxygen and hydrogen. It seems impossible that other substances could be present. In the first place the original material used was a pure sucrose. During the process of carbonization it came into contact with nothing but pure silica, platinum and agate. Pure alcohol was used as the source of heat and the charred material was held at red heat for five to ten minutes, during which time it was so thoroughly stirred that all particles were exposed to the air. It is hardly probable that any organic decomposition products could have withstood the treatment. Since no inorganic matter was originally present, and from the precautions taken there was little likelihood of any being introduced during the manipulation, it seems safe to assume that the product finally obtained must have been in a high state of purity.

Two membranes were prepared from this material. The cavity in the cell was filled by sucking material through in a water suspension. The cake so formed was pressed and the pores clogged with a suspension of finer material. Much difficulty was encountered with these membranes and the above process had to be repeated many times before a membrane was obtained which gave signs of osmotic activity. The membranes were pressed, measured and tested with water alone and then with $M/1$ sugar solution on one side until osmotic effects were observed. No. 6 failed to show signs of such effects with approximate pore diameters of 1.976 microns and No. 11 with pores measuring 1.185 microns in diameter. The following figures were obtained with cells when the pore diameters had been reduced to 1.185 and 0.423 microns, respectively:

TABLE 9
M/2 sugar solution
No. 6

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
3/3	0	9	3/10	23	32
3/4	13	22	3/12	25	34
3/5	15	24	3/13	26	35
3/6	16	25	3/15	27	36
3/7	19	28	3/16	27	36
3/9	21	30			

No. 11

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
3/ 7	0	9	3/11	1	10
3/ 9	1	10			

M/1 sugar solution
No. 6

3/17	0	17	3/25	6	23
3/19	3	20	3/27	7	24
3/20	4	21	3/28	7	24
3/24	5	22			

No. 11

4/ 3	0	17	5/16	79	96
4/ 5	8	25	5/20	85	102
4/10	18	35	5/25	92	109
4/14	27	44	6/ 2	102	119
4/18	34	51	6/ 7	106	123
4/22	41	58	6/13	112	129
4/27	49	66	6/20	117	134
5/ 2	57	74	6/23	119	136
5/ 6	64	81	6/28	122	139
5/11	71	88	6/30	122	139

2 M sugar solution

No. 6

3/28	0	31	4/ 4	8	39
3/29	—2	29	4/ 5	10	41
3/30	0	31	4/ 6	12	43
3/31	0	31	4/ 7	14	55
4/ 1	2	33	4/ 9	17	48
4/ 2	4	35	4/10	17	48
4/ 3	6	37			

No. 11

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
6/30	0	31	7/14	28	99
7/ 1	4	35	7/15	73	104
7/ 3	15	46	7/17	81	112
7/ 5	25	56	7/18	86	117
7/ 6	31	62	7/19	91	122
7/ 7	36	67 ¹	7/21	103	134
7/ 8	38	69	7/22	102	133
7/10	51	82	7/24	102	133
7/11	55	86			
7/12	60	91			
7/13	64	95			

The cells were taken apart and the membranes washed out, clogged with fine material and again pressed at 350 kg per cm² for several hours. They then gave the results shown in the following tables:

TABLE 10
M/2 sugar solution
No. 6

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
6/ 5	0	9	6/ 9	30	39
6/ 6	9	18	6/10	34	43
6/ 7	18	27	6/12	37	46
6/ 8	25	34	6/13	37	46

¹ Bath temperature rose 1° here.

No. 11

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
8/12	0	9	11/ 5	105	114
8/14	4	13	11/11	110	119
8/23	15	24	11/17	116	125
8/30	21	30	11/24	120	129
9/ 9	33	42	11/29	125	134
9/18	45	54	12/ 5	128	137
9/30	62	71	12/11	133	142
10/ 6	69	78	12/17	137	146
10/12	77	86	12/22	140	149
10/18	85	94	12/24	142	151
10/24	92	101	12/31	146	155
10/30	99	108	1/ 3	142	151

M/1 sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
6/14	0	17	6/21	50	67
6/15	8	25	6/22	52	69
6/16	20	37	6/23	55	72
6/17	30	47	6/24	57	74
6/19	42	59	6/26	57	74
6/20	47	64			

No. 11

1/ 5	0	17	2/26	110	127
1/ 6	4	21	3/ 3	119	136
1/11	21	38	3/ 8	127	144
1/16	30	47	3/13	136	153
1/21	40	57	3/18	145	162
1/26	50	67	3/23	152	169
2/ 1	62	79	3/28	159	176
2/ 5	71	88	3/31	163	180
2/10	81	98	4/ 5	170	187
2/15	90	107	4/11	177	194
2/20	100	117			

2 M sugar solution
No. 6

6/26	0	31	7/ 7	138	169
6/27	18	49	7/ 8	146	177
6/28	34	65	7/10	162	193
6/29	50	81	7/11	170	201
6/30	62	93	7/12	177	208
7/ 1	94	125	7/13	184	215
7/ 3	97	128	7/14	191	222
7/ 5	118	149	7/15	200	231
7/ 6	128	159	7/17	214 ¹	245

Flaky graphite: The flaky graphite used in preliminary work was subjected to much the same treatment in purification as was the "Aquadag." It was digested several times with HCl and with HNO₃, washed thoroughly after each digestion with hot water until free from acid and finally it was treated twice with HF. After washing and drying it analyzed as follows for loss on ignition:

a. 0.6409 g : 0.0001 g residue : 100.00% volatile

b. 0.7969 g : 0.0005 g residue : 99.98% volatile

Av. = 99.98% volatile

Owing to the small amount of material, only one membrane was made up. It was repeatedly pressed at 350 kg per cm² and tested for osmotic activity but showed none until the pore diameters had been reduced to 0.494 micron when it gave the following:

TABLE II
2 M sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
2/22	0	31	3/ 8	3	34
2/28	1	32	3/12	4	35
3/ 4	3	34	3/14	4	35

Copper: The material for this work was at first purified by shaking out repeatedly with petroleum ether. It analyzed as follows:

0.2196 g subst.; 33.0 cc N/10 Na₂S₂O₃; 99.15% Cu.

¹ Further readings impossible owing to level of solvent sinking into cell.

One membrane was made from it by pressing at 300–350 kg per cm² for approximately sixty hours. It showed pores having maximum diameter of 0.741 micron. When this membrane was set up with *M*/1 sugar solution on one side and the water and solution levels were equalized, the latter sank till a value of 0, corrected for density, was attained.

Subsequent pressings reduced the maximum pore diameters to 0.423 micron when it gave the following results with 2 *M* sugar solution:

TABLE 12

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
3/ 4	0	31	3/10	10	41
3/ 5	3	34	3/11	11	42
3/ 6	5	36	3/12	13	44
3/ 7	6	37	3/13	13	44
3/ 8	7	38	3/14	13	44
3/ 9	7	38			

Later the impure copper powder was ignited and then reduced by heating in an atmosphere of hydrogen. This product analyzed as follows:

0.8689 g subst.; 1.0838 g CuO; 99.65% Cu

The following results were obtained with two of the membranes prepared from it by pressing at 350–400 kg per cm² for several days:

TABLE 13
M/2 sugar solution
No. 5

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
3/15	—3	6	3/19	—6	3
3/16	—5	4	3/20	—7	2
3/17	—5	4	3/21	—7	2
3/18	—6	3			

No. 16

3/ 3	0	9	3/ 6	—7	2
3/ 4	—4	5	3/ 7	—7	2
3/ 5	—6	3			

M/1 sugar solution
No. 5

3/22	—8	9	3/25	—12	5
3/23	—10	7	3/26	—12	5
3/24	—12	5	3/27	—13	4

No. 16

3/ 8	—4	13	3/14	—14	3
3/ 9	—8	9	3/15	—14	3
3/10	—9	8	3/16	—16	1
3/11	—11	6	3/17	—16	1
3/12	—13	4	3/18	—15	2
3/13	—14	3	3/19	—15	2

2 *M* sugar solution
No. 5

3/28	16	47	4/ 1	32	63
3/29	24	55	4/ 2	33	64
3/30	28	59	4/ 3	33	64
3/31	31	62	4/ 4	33	64

No. 16

3/20	10	41	3/24	17	48
3/21	16	47	3/25	16	47
3/22	18	49	3/26	14	45
3/23	18	49	3/27	14	45

After washing, pressing, and saturating the membranes they were again set up in the cells. The following results were observed:

TABLE 14
M/2 sugar solution
No. 5

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
4/12	0	9	4/14	8	17
4/13	10	19			

No. 16

4/12	0	9	4/14	4	13
4/13	5	14			

M/1 sugar solution

No. 5

4/24	0	17	4/26	10	27
4/25	7	24	4/27	9	26

No. 16

4/24	0	17	4/26	7	24
4/25	5	22	4/27	6	23

2 M sugar solution

No. 5

4/30	0	31	5/ 6	65	96
5/ 1	19	50	5/ 7	68	99
5/ 2	34	65	5/ 8	71	102
5/ 3	45	76	5/ 9	73	104
5/ 4	54	85	5/10	74	105
5/ 5	60	91	5/11	74	105

No. 16

4/30	0	31	5/ 6	60	91
5/ 1	16	47	5/ 7	63	94
5/ 2	30	61	5/ 8	66	97
5/ 3	42	73	5/ 9	68	99
5/ 4	50	81	5/10	69	100
5/ 5	56	87	5/11	70	101

Silver: The material was prepared by dissolving pure silver chloride in ammonia and precipitating with HCl. This process was repeated several times. The silver chloride was reduced as before. The resulting product was treated with ammonia to dissolve any unreduced salt and analyzed. It gave the following results:

0.4200 g subst.; 0.5574 g AgCl; 99.93% Ag

A membrane was prepared by pressing at 200 kg per cm² but failed to show signs of osmotic activity. It was alternately pressed at 350 kg per cm² and tested until the pore diameters were less than 0.329 micron. Their exact magnitude was undeterminable owing to the high pressure required to displace the water in the pores. The following results were observed:

TABLE 15
M/2 sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
6/14	0	9	6/17	—3	6
6/15	5	14	6/19	—7	2
6/16	0	9			

M/1 sugar solution

6/20	0	17	6/22	—6	11
6/21	2	19	6/23	—10	7

2 *M* sugar solution

6/28 9 A.M.	0	31	6/29	21	52
6/28 5 P.M.	17	48	6/30	14	45

The membrane was washed, pressed, and after testing with water, was again set up with sugar solution. It gave the following results:

TABLE 16
Silver membrane *M*/2 sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
7/13	0	9	7/15	15	24
7/14	26	35			

M/1 sugar solution

7/17 11 A.M.	0	17	7/18	8	25
7/17 5 P.M.	4	21	7/19	8	25

2 *M* sugar solution

7/24	0	31	7/27	28	59
7/25	6	37	7/28	31	62
7/26	19	50	8/1	25	56

Gold: The membrane giving the following results was prepared as previously described except that the rubber packing was replaced by paraffined filter paper. The material was purified as before. The membrane when formed weighed 13.5 g and was between 3 and 4 mm thick. Owing

to the presence of one large pore which caused the formation of bubbles which interfered with the observations, the pore diameter measurements of this membrane were not made. The pore diameters were not greater than 0.984 micron however. The following results were noted:

TABLE 17
Gold membrane $M/2$ sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
3/ 3	0	9	3/ 6	3	12
3/ 4	1	10	3/ 7	3	12
$M/1$ sugar solution					
3/15	0	17	3/17	—1	16
3/16	—1	16			
2 M sugar solution					
4/ 1	0	31	4/ 7	8	39
4/ 2	4	35	4/ 9	9	40
4/ 3	6	37	4/10	8	39
4/ 4	6	37			
4/ 5	7	38			

The membrane was washed and again pressed at 200 kg per cm^2 for an hour and half. The pores then were less than 0.912 micron in diameter. It gave the following results:

TABLE 18
 $M/2$ sugar solution
No change in level. Corrected reading = 9 mm
 $M/1$ sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
5/ 1	0	17	5/ 6	4	21
5/ 2	1	18	5/ 8	5	22
5/ 4	3	20	5/10	5	22
2 M sugar solution					
5/10	0	31	5/13	5	36
5/12	3	34			

After another pressing which reduced the pore diameter to less than 0.591 micron, it gave the following results:

TABLE 19
M/2 sugar solution

	Readings			Readings	
	Observed	Corrected		Observed	Corrected
6/30	0	9	7/ 5	5	14
7/ 1	2	11	7/ 6	5	14
7/ 3	4	13			

M/1 sugar solution

7/ 6	0	17	7/ 8	5	22
7/ 7	4	21	7/10	6	23

2 *M* sugar solution

No change in level. Corrected reading = 31 mm

Discussion

The above results are summarized in the Table 19 which contains the maximum observed readings. They possess only a rough quantitative value since in many cases the maximum possible reading was not obtained because the rate of change became too slow to warrant the expenditure of time necessary for the cell to reach equilibrium. In a general way, however, the figures are comparable. In case results are cited with two different membranes, the fact is indicated by the headings Cell A and Cell B. As was previously stated, the general method of conducting the experiments from which these results were obtained was as follows:

When the membrane had been pressed it was set up with water on both sides. If no change in the levels of the liquid resulted the water on one side was replaced with *M/2* sugar solution. The resulting reading is that given in column *a* under *M/2* sugar solution. The cell was next taken apart, the faces of the membrane washed off with distilled water and the cell set up with *M/1* sugar solution in place of the *M/2* solution. The reading thus obtained is recorded in column *a* under the corresponding sugar solution. The same procedure

was followed in obtaining the a reading for the $2 M$ solution. When this last reading had been taken, the cell was taken apart and the membrane washed out by forcing distilled water through it, after which it was pressed as indicated in the descriptions of the various experiments. It was then again set up with water on both sides and, if no change in level occurred, put through the same procedure as above, giving the values recorded in the b columns. Thus the readings in columns a and b with any one membrane indicate the results obtained with this membrane before and after reducing the diameters of its pores. In other words, the b readings represent the results with membranes having pores of smaller diameters than the membranes giving the corresponding a readings but differing from them in no other respect.

TABLE 20
Preliminary Experiments

Solution	SiO ₂	Tech. graphite	"Aquadag"	Sugar carbon	Flaky graphite	Copper	Silver		Gold				
							a	b	a	b	c	d	e
$M/2$ sugar	—	—	—	—	—	—	—	—	—	—	—	13	14
$M/1$ sugar	28	25	58	86	35	20	10	28	6	11	197	32	17
$2 M$ sugar	—	—	—	—	110	35	—	—	—	—	—	68	103

Final Experiments

Solution	Cell A						Cell B					
	$M/2$ sugar		$M/1$ sugar		$2 M$ sugar		$M/2$ sugar		$M/1$ sugar		$2 M$ sugar	
	a	b	a	b	a	b	a	b	a	b	a	b
Silica	23	65	72	202	110	308+	66	—	113	—	267+	—
"Aquadag"	16	—	85	—	200	—	37	30	28	60	184	234
Sugar carbon	34	46	24	74	48	245	10	155	139	194+	133	—
Flaky graphite	12	—	25	—	—	—	—	—	—	—	—	—
Copper	6	19	9	27	64	105	9	14	13	24	49	101
Silver	14	35	19	25	52	62	—	—	—	—	—	—
Gold	12	9	17	22	40	36	—	—	—	—	—	—

Bearing of the Results on the Cause of Osmosis and the Function of the Semipermeable Membrane

In the review of the literature given in the first pages of this article the theories concerning the cause of osmosis may be divided into comparatively few classes, namely those attributing osmosis to.

1. A difference in the surface tension of solvent and solution.
2. A difference in the solubility of the solvent and the solution in the membrane.
3. An attraction of the solute molecules for the solvent molecules.
4. The so-called kinetic theory.
5. A difference in the vapor pressures of the solvent and solution.
6. A chemical reaction between the membrane, solvent and solution.
7. A difference in electrical potential between the opposite faces of the membrane.

The advocates of these theories and their various modifications advanced them as applying to osmotic phenomena in general and, if later, certain exceptions were found for any one theory, that theory was thrown into more or less disrepute. The main endeavor of investigators has been to find *one* theory to explain osmosis, by osmosis being meant the flow of one liquid through a membrane permeable for it, into another liquid, for which the membrane is less permeable, until a certain difference in hydrostatic pressure is produced on opposite sides of the membrane. Yet the conditions under which "osmosis" takes place differ greatly in different experiments.

Thus, membranes range from a layer of liquid to a layer of solid such as metallic gold or unglazed porcelain and include rubber, parchment and various other animal, vegetable and inorganic membranes. The liquids used in producing osmosis vary as widely in character. When these things are considered it seems improbable that the phenomena in question should all be traceable to a single cause. It is more probable

that we are dealing with several which manifest themselves in the same way, *i. e.*, in causing a transference of liquid through the membrane. Nor is this contrary to experience. In a "three-liquid layer" experiment for instance, the force is undoubtedly the difference in the "attraction of solution" between the liquids involved. The corresponding result may be brought about with a porous wall and two solutions under the influence of an electric current, *i. e.*, in electric osmose. Yet in the latter case we have no "attraction of solution" between the liquids and the membrane. In the case of sugar solution and water separated by a membrane of unglazed porcelain we have but little evidence of either of these forces being operative. The difference between ordinary osmosis and electrical osmose is that in the former the energy is derived from the system itself while in the latter it comes from an external source. That this same kind of energy may also be developed internally for the production of strictly analogous phenomena is fairly evident from Bartell's work on "negative osmose."¹

If we grant then that "attraction of solution" may produce osmosis in a three-liquid layer experiment and difference in electrical potential may produce it in either electrical osmose or "negative osmose," we have differentiated "osmose" into at least two phenomena and, unless we conceive of "solution" as the filling of membrane pores of capillary dimensions with the liquid, we must apparently admit the existence of still a third class of osmotic phenomena obtainable with aqueous solutions of sugar, water and membranes of the inert materials used in the present work. Many of the various theories advanced appear plausible under certain circumstances and the fact that they are not always so should not cause their complete rejection. For instance, the relationships between surface tension and osmotic effect pointed out by Traube² seem to consistent to be attributed to coincidence and their significance should not be entirely denied because Barlow³

¹ Jour. Am. Chem. Soc., **36**, 646 (1914).

² Phil. Mag., (6) **8**, 704 (1904).

³ Ibid., (6) **10**, 1 (1905).

later found them incapable of universal application. It is quite conceivable that difference in surface tension should under some circumstances produce liquid movements across a diaphragm but it is quite unnecessary to conclude therefrom that all such movements are due to this cause. It is equally absurd to postulate that since this explanation is not always tenable it is never so. It seems fairly obvious therefore that osmosis may be due not to one but to a variety of causes.

Nevertheless, several of these groups of theories which ascribe to the membrane an active role in the phenomena of osmosis and which are apparently at first sight irreconcilable, prove to be, upon closer scrutiny, very closely related to each other.

According to these theories osmosis takes place:

1. Through capillary spaces in the membrane,
2. By the solution of the solvent in the membrane, and
3. By the formation of a labile chemical compound between the membrane and the solvent.

That osmosis can take place through capillaries, as distinguished from molecular interstices, seems probable from the fact that it has been observed to occur when two liquids are in contact only through fine cracks in glass tubes,¹ through the pores in unglazed porcelain, through the various membranes described by Tinker² and through those used in the experiments reported in the present article. The limits of these pore diameters between which osmosis can take place are not definitely known but Bigelow and Bartell³ and Bartell⁴ have shown that with unglazed porcelain clogged with various materials the upper limit seems to be about 0.9 micron, a figure much too large to represent the dimensions of molecular interstices. This work has been corroborated by Tinker⁵ and is in agreement

¹ See in this connection, Fischer: *Pogg. Ann.*, **10**, 481 (1827); Dutrochet: *Ann. Chim. Phys.*, **35**, 383 (1827); **49**, 411 (1832); Brucke: *Pogg. Ann.*, **58**, 77 (1843).

² *Loc. cit.*

³ *Jour. Am. Chem. Soc.*, **31**, 1194 (1909).

⁴ *Jour. Phys. Chem.*, **15**, 318 (1911); *Dissertation*, Univ. of Mich., 1910.

⁵ *Loc. cit.*

with that of Draper¹ on osmosis as applied to gases. That the lower limit may be of the dimensions of molecular interspaces is equally certain from the results of various investigators who have used the three-liquid layer arrangement, and in these cases there is certainly a solution of the liquids in the membrane.

The validity of the last of the three suggestions, namely the formation of a labile chemical compound between the membrane and the solvent, has not been so certainly demonstrated. It is however a possibility as will appear later.

As has been pointed out by Bigelow,² these views have always been held to be "mutally exclusive," although this was not at all necessary and in reality it is possible to bring them all into harmony. He showed that "the rate of passage of liquids through molecular interstices is expressible by the same laws which formulate the rate of passage of liquids through capillary tubes," thus affording experimental proof that there is no essential difference between capillaries and molecular interstices in this respect. Theoretically, interspaces of all dimensions from macroscopic capillaries down to infinitely small interstices are capable of existence. All phenomena which result from forces inherent in such interspaces should also manifest themselves and furthermore in a continuous fashion except as they may be influenced by certain secondary factors. There is really no basis for assuming that between the pores of solid membranes of capillary structure on the one hand and the molecular interspaces of liquid membranes on the other there exists a region of osmotically inactive spaces. It is far more logical to suppose that osmotic phenomena with the membranes are but extremes of one and the same process. From this it follows that there is no sharp line between the changes occurring in ordinary capillaries and in intermolecular interstices.

Furthermore, it is entirely conceivable that in the latter category may be included the formation of certain chemical compounds such, for instance, as certain so-called molecular

¹ Jour. Franklin Inst., 17, 177 (1827).

² Jour. Am. Chem. Soc., 29, 1690 (1907).

compounds. Some investigators, while apparently realizing this, have failed to apply it to the phenomena in question with the possible exception of Lhermite.¹ Thus Graham² admits "that chemical affinity of the lowest degree may shade into capillary attraction" and Fitzgerald³ states that "When we come to deal with really molecular magnitudes it is impossible to draw a hard and fast line between physical and chemical permeability." For many years there has been accumulating in chemical literature, evidence in support of this view in the tendency to class solution processes with chemical reactions and many investigators have pointed out that some of the criteria of the formation of true chemical compounds apply equally well to certain of these processes.

It appears evident, therefore, that there may not be such an impassable gulf between the capillary solution and chemical theories of the membrane function as their respective advocates have believed.

Effects of Various Factors on the Efficiency of Osmotic Membranes

As mentioned above, the experiments described in the present report demonstrate conclusively that osmotic pressure can be obtained through the action of capillary attraction alone without the aid of either solution or chemical action. Theoretically, a certain solution tendency must be ascribed to all metals, even including metallic gold, but it is scarcely conceivable that such solubility effects could produce osmotic pressure and this conception is still more difficult in the case of carbon which apparently differs in no way from the other materials as regards its action as an osmotic membrane. From these considerations, ordinary solution effects may be excluded as the universal cause of osmosis.

Effect of the size of the pore diameters: If, then, in certain cases, the manifestation of osmotic pressure is de-

¹ Loc. cit.

² Phil. Trans., **151**, 222 (1861).

³ Jour. Chem. Soc., **69**, 897 (1896).

pendent upon the continuous state of the membrane, it would seem to be a necessary consequence that the magnitude of the results should increase with the decrease in the diameters of the pores of the membrane until these diameters became so small as to offer resistance to the passage of the molecules of the liquid. Assuming for the moment that all the pores in the membrane have the same diameter, it would be expected that, with pores of larger diameters than those at which the molecules of the liquid meet with resistance in their passage through the membrane, both the magnitudes of the results obtainable and rates of flow of liquid would continue to increase with decrease in the pore diameters, but that, when these pore diameters became small enough to offer resistance to the passage of the liquid, the rate of flow of the liquid would diminish. Finally a point would be reached at which the membrane would become impervious to the liquid. At this point the magnitude of the osmotic effects would reach a maximum but the velocity at which this maximum would be reached would be infinitely small. On the other hand, if the pores of the membrane are not all of the same diameter, a condition which, of course, is the one existing in the membranes used in the present work, the results obtained would represent the resultant of the action of pores ranging in diameter from those just small enough to give osmotic effects to those giving the maximum effects. When the membranes are pressed or the pores clogged the number of pores capable of giving osmotic effects is increased and the diameters of those already showing osmotic activity are decreased, with the result that the total magnitude of the osmotic effect is at first increased. As the process is carried further, however, more and more pores will become impervious to the liquid while these still permeable will permit only a slow passage of liquid and thus a gradual decrease in the observed effect will result. In brief then, as the diameters of the pores of a membrane are progressively decreased we should expect the osmotic pressure produced to increase to a maximum and then decrease to nil as the membrane finally becomes impervious to the liquid.

In Table 19 it will be observed that in practically all cases the *b* reading is larger than the corresponding *a* reading. Since, between the taking of these two readings, the membranes were pressed and in some cases clogged with fine material, it may be safely assumed that the *b* readings were made with membranes having smaller pores than those giving the corresponding *a* readings. Apparently then, for the ranges of pore diameters in these experiments, osmotic activity does increase with a decrease in pore diameters.

That the osmotic pressure finally reaches a maximum and then decreases is indicated by the results obtained with the gold membrane used in the preliminary experiments with which successive compressions of the membrane caused it to give osmotic pressures of 6, 11, 197, 40 and 25 mm, respectively. It is possible that this accounts for the small effects noted with the second gold membrane which was prepared and used in the later work. This membrane was subjected to somewhat higher pressures than was the former one and appeared to be much denser. The same is true of some copper membranes prepared for the second series of experiments. These results are substantiated by the actual measurements of the pore diameters.

It must be distinctly understood, however, that the importance of the pore diameter measurements in this work must not be overestimated. The values given represent only the diameters of the largest pores and these constituted but a small proportion of the total number in the membrane. The following table shows the smallest of these maximum values at which positive effects were obtained with the various materials:

TABLE 21

Material	Pore diameter	Material	Pore diameter
Silica	0.349 micron	Copper	0.423 micron
Aquadag	0.593 micron	Silver	0.329 micron
Sugar carbon	0.423 micron	Gold	0.984 micron
Flaky graphite	0.494 micron		

But whatever the actual sizes of the largest pores which exhibit osmotic activity, the first effect of reducing their sizes is to cause an increase in the osmotic pressure produced by them.

Effect of the chemical composition of the membrane: This factor is perhaps the most important one from the standpoint of this investigation, since its study was the original aim of the work herein described. The results obtained show, as do those of Bigelow, Bartell, and Tinker that there is a relation between the physical condition of the membrane and the osmotic effects obtained, but that the influence of the chemical composition of the membrane is, at most, of secondary importance. They also show that chemical reactions, in the ordinary sense of the term, between the membrane and the liquids bathing it are certainly not the only deciding factors in the manifestation of osmotic phenomena. The results with silica are perhaps inconclusive because of its tendency to combine with water to form silicic acid and because its well known colloidal properties may make possible certain complications. Such considerations, however, seem scarcely applicable to metallic gold and silver and to carbon, all of which apparently differ in no way from each other and from other materials as regards their action as osmotic membranes. The very universality of the ability of substances to act as semipermeable membranes argues against this property being due entirely to the chemical constitution of these substances. It seems to be a property more colligative than constitutive in its nature.

Effect of concentration of the solution: A study of Table 19 shows that, as would be expected, the magnitude of the observed osmotic effects increases with an increase in the concentration of the sugar solution, other factors, of course remaining constant. In some cases, however, surprisingly large values were noticed with the 2 *M* solution as compared with the other two. While an increase would be expected, such a distinct difference in behavior of two solutions as concentrated as *M*/1 and 2 *M* was rather surprising. It may be

that this is a scrap of experimental evidence in support of those theories which postulate that the size of the liquid units in solution exceed those in the pure solvent and are responsible in some cases, for the phenomena of osmosis.¹ This suggestion assumes an added importance in the light of the work of deBruyn and Wolff² whose results indicate that concentrated sugar solutions exhibit some of the properties of colloidal solutions, notably the Tyndall effect. Inasmuch as the particles which produce such effects are usually considered to exceed molecular dimensions, *i. e.*, to consist of molecular aggregates, it may be concluded that in such concentrated solutions we are dealing, not with single molecules of water and of sugar, but with masses consisting either of sugar molecules alone or of sugar molecules which have attracted to themselves water molecules to form a hydrated complex.

These statements are offered merely as suggestions since obviously the experimental data are altogether too scanty to permit positive conclusions being drawn.

Summary

The results of the investigations reported in this paper may be briefly summarized as follows:

1. A method and apparatus have been devised for the study of osmotic phenomena with membranes of powdered materials.
2. Osmotic effects have been obtained with materials which have heretofore never been used successfully for this purpose, *viz.*, silica, amorphous carbon, graphite and metallic copper, silver, and gold.
3. The results of other investigators indicating that the magnitude of osmotic effects increases with a decrease in the diameters of the pores of the membrane have been corroborated.
4. It has been demonstrated that osmotic pressure can be produced through the agency of capillary forces alone without the aid of solution processes or chemical reactions.

¹ See in this connection references to work of Pickering and of Poynting on pages 3 and 4, respectively.

² Rec. Trav. chim. Pays.-Bas., **23**, 155 (1904).

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